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13. ABSTRACT (Maximum 200 words)

This research concerned the development of theoretical tools to design optical fields for the manipulation of molecular-scale dynamical events. Key advances emanating from this research are as follows:

(1)   The rigorous foundations for control of quantum phenomena were established.
(2)   A family of numerical algorithms was created for implementing laser designs for manipulating molecular motion.
(3)   It was demonstrated that adaptive feedback control at ultrafast molecular time scales can overcome inherent theoretical and laboratory uncertainties.
(4)   Foundations for a comprehensive algorithm for control, as well as inversion, of molecular dynamical processes was established as a basis for future research.

The report highlights these developments, as well as a variety of inter-related advances in the domain of molecular control theory. The results of this study are expected to open up ensuing laboratory research in the field.

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SUMMARY OF RESEARCH ACCOMPLISHMENTS

Below are highlighted the particular molecular control advances achieved in this research:

1. **Optimal Control of Nonlinear Classical Systems with Application to Unimolecular Dissociation Reactions and Chaotic Potentials.[1]**

   This research applied optimal control theory to nonlinear classical systems, for the design of electric fields that interacted with the systems so that an ensemble of classical trajectories were manipulated in some desired way. Control of selective unimolecular bond dissociation was demonstrated in the classical regime, on a model linear triatomic molecule, with spreading of the ensemble of trajectories held to a minimum for closer agreement between quantum and classical mechanics. Control was also demonstrated over trajectories in a highly chaotic two-dimensional system. It was found, in the cases studied, that a high degree of control was attained in situations where the dynamics were chaotic in the absence of a controlling field.

2. **Optimal Control of Molecular Motion: Making Molecules Dance.[2]**

   This work presented an overview of the recent incorporation of formal control theory concepts into molecular physics. The desire to control molecules has a long history, and it was argued that the tools for control theory provided a rigorous foundation for precisely expressing the physical issues, as well as providing a practical means for obtaining solutions, when they exist. The process involved was one of design, and the choices and flexibility to the molecular control designer were emphasized. Illustrations were included, involving the control of molecular rotation, vibration, and dissociation. The work attempted to present a synopsis of the current status of the field, and where it will likely proceed.

3. Optimal Control of Molecular Motion.[3]

The work presented an overview of recent developments concerning the introduction of optimal control techniques into the molecular domain. The goal of this research was to identify the degree to which molecular dynamics may be controlled by external optical fields, and provide a systematic means for designing optical fields for this purpose. Preliminary illustrations of molecular optimal control theory were considered, involving rotational, vibrational, and electronic degrees of freedom. With the ultimate objective being laboratory implementation of the designed fields, the robustness of the designs was a critically important issue. These various topics were reviewed in this work.

4. Optimal Control of Selectivity of Unimolecular Reactions Via An Excited Electronic State with Designed Lasers.[4]

In this study, a molecular system was steered on the ground electronic surface, from the initial state to a desired target time T via an excited electronic state, by using optimal designed coherent laser fields. A new algorithm based on the SU(2) algebra was developed to solve the time-dependent Schrödinger equation for the systems involving two electronic states with time-dependent Hamiltonians. For the design of optimal fields with restricted functional forms, the rotating wave approximation was introduced for significantly reducing the computational effort. As a model of unimolecular reactions, a double-well switching problem was studied. The objective was to move the system from one well to the other. It was found that the unrestricted optimal fields which successfully moved the system from one well to the other at the target time T were complicated. The objective was achieved through the cooperative interaction between the system and the driving field. The optimal fields with restricted functions forms, such as a train of Gaussian pulses with a single carrier frequency, could also lead to the satisfactory achievement of the objective. However, except for some propitious cases, a simple two-pulse pump-dump scheme did not achieve the control objective satisfactorily. Possible further potential applications were discussed briefly.

5. Robust Optimal Control Theory for Selective Vibrational Excitation in Molecules: A Worst Case Analysis.[5]

Recent research has demonstrated that optimal electromagnetic fields, capable of producing selective vibrational excitation in molecules, can be designed employing linear quadratic control methods using a cost functional that balances the energy distribution in the molecule, the fluence of the optical field, and a final cost to insure the desired excitation. Practical computations of molecular control theory for large molecules, especially with anharmonic potentials, become difficult to obtain due to the increased dimensionality and the accompanying uncertainty in the Hamiltonian. In this work, we reduced the complexity of the problem by treating a portion of the molecule, including the target and optical dipoles, in full detail, while the remainder of the molecule was modeled as an external disturbance of bounded energy. The optimal control field now *minimized* the cost functional, which is simultaneously *maximized* with respect to the energy constrained external disturbance to assure robustness. This optimal design process was commensurate with taking the most pessimistic view of the disturbance. This conservative view was born out in the numerical calculations, such that practical laboratory studies could reach results much improved over the worst case design. As an illustration, we investigated disturbances of varying energy content for a truncated 20-atom molecular chain, where the uncontrolled remainder of the chain was the source of the system disturbance. The sensitivity of the system with respect to the disturbance was found to be strongly dependent on the distance of the disturbance to the target bond and the dipole arrangement. In addition, in the range of physically reasonable disturbance energy, the optimal field could be accurately predicted from an asymptotic expansion involving only the reference undisturbed case. Although this work took advantage of linear system techniques, the same robust optimal control procedure could be generalized to nonlinear systems by a variety of means.

6. **Application of the Born-Oppenheimer Principle to Classification of Time Scales in Molecules Interacting with Time-Dependent External Fields.[6]**

In this study, an analysis of the Hamiltonian of a molecule interacting with time-dependent external fields led to the identification of various time scales governing the motion of electrons and the nuclei. The most important role was played by the Born-Oppenheimer approximation, which considered the nuclear kinetic to be bounded and small, compared to the gradient of the electronic potential surfaces. The relative electronic-excitation operator was defined, and was shown to be slowly dependent on time. This was a consequence of the Born-Oppenheimer approximation, in the context of the time-dependent Schrödinger equation, and the interaction with an external electric field. It was shown how to capitalize on this identified slow motion in the presence of rapid Rabi oscillations driven by the external field. The stroboscopic-integration technique was used in an illustrative calculation, for the case of two electronic states coupled by the external field.

7. **Optimal Control of Curve-Crossing Systems.[7]**

This work examined controlling curve-crossing dynamics of a model diatomic system between two dissociative electronic states through radiative coupling with a third bound state. Starting with an initial wavepacket on one of the crossing surfaces, optimal control theory was used to design the radiative field to either enhance or eliminate (at our choice) selectivity of one product channel over another. A new optimization procedure was introduced which filtered out dc and low frequency components from the optimal field, but still allowed for resonant transitions to a third bound state. This procedure forced the fields to employ interesting physical mechanisms involving the bound state, in order to control the electronic branching ratios, rather than directly negating or enhancing the diabatic coupling term in the Hamiltonian. A new propagation scheme for a multisurface Hamiltonian, using Pauli matrices, was also presented.

8. Coherent Control of Quantum Dynamics: The Dream is Alive.[8]

In this work, current experimental and theoretical progress toward the goal of controlling quantum dynamics was summarized. Two key developments have now revitalized the field. First, appropriate ultrafast laser pulse shaping capabilities have only recently become practical. Second, the introduction of engineering control concepts has put the required theoretical framework on a rigorous foundation. Extrapolations to determine what is realistically possible were presented.

9. Optimally Controlled Quantum Molecular Dynamics: A Perturbation Formulation and the Existence of Multiple Solutions.[9]

This work considered optimal control of quantum mechanical systems within the framework of perturbation theory, with respect to the controlling optical electric field. The control problem was expressed in terms of a cost functional including the physical objective, the penalties, and constraints. The resultant nonlinear variational equations were linearized by considering the lowest-order term in an expansion in the powers of the optical field strength. The optical field was found to satisfy a linear integral equation, and the solution could be expressed in terms of a generalized eigenvalue problem associated with the corresponding kernel. A full determination of the field was specified through the solution to the integral equation and the roots of an accompanying linearized spectral equation, for a characteristic multiplier parameter. Each discrete value of the latter parameter corresponded to a particular solution to the variational equations. As a result, it was argued that under very general conditions, there would be a denumerably infinite number of solutions to well-posed quantum mechanical optimal control problems.

10. **Optimally Controlled Quantum Molecular Dynamics: The Effect of Nonlinearities on the Magnitude and Multiplicity of Control-Field Solutions.[10]**

This work addressed the nature and multiplicity of an optimally designed electric field for controlling quantum dynamical processes. A rather general cost functional was considered, with only mild conditions called for amongst the various operators involved. An explicit upper bound on the magnitude of the controlling electric field was attained, in terms of the norms of various operators entering into the control cost functional. An earlier work employing first-order perturbation theory arguments showed that, under rather mild assumptions, a denumerably infinite number of control field solutions exists for the optimal control problem. This study showed that through a bound on the remainder of the nonlinear terms in the expansion, this same conclusion concerning the control field multiplicity continues to hold.

11. **Optimal Control of the Electric Susceptibility of a Molecular Gas by Designed Non-resonant Laser Pulses of Limited Amplitude.[11]**

This work presented a theoretical study on optimal control of electric susceptibility change of a homogeneous molecular gas, resulting from orientational anisotropy induced by nonresonant lasers with limited intensity. It was assumed that the molecular gas was initially in thermal equilibrium. Two types of optimal control objectives were considered: (a) terminal control, and (b) temporal profile control (i.e., trajectory control). A step function was introduced into the cost functionals, which successfully helped to realize the restriction on the magnitude of the field amplitude in numerical optimization, as demonstrated by the examples. Calculations were carried out for CS_2, which has a small rotational constant (B - 0.1091 cm^{-1}) and a quite large polarizability anistropy ($\Delta\alpha = 9.6$Å^3). For terminal control of a maximal susceptibility change at a target time T, it was found that the optimal control field was composed of a series of rectangular pulses with identical amplitudes equal to a preassigned bound value. All of the optimal fields for terminal control are functions of (T −

t) over the time interval [0,T], with characteristic time 1/8 B and period 1/2 B. For temporal profile control, the degree of control was strongly dependent on the length of time interval over which a target profile is defined. Usually, if a time interval was shorter than 1/8 B and a target profile was a smooth and non-negative function with a reasonable maximal value, the control could be achieved perfectly. In other cases, the detailed assignment of the weight function in the cost functional played an important role in determining how to make an optimally controlled susceptibility change profile approach the target profile. Furthermore, this work also examined the temperature effects on optimal control. It was shown that the general optimal control properties observed by CS_2 will also be valid for other nonlinear molecular gases with small rotational constants.

12. Inverse Quantum-Mechanical Control: A Means for Design and a Test of Intuition.[12]

The inverse quantum mechanical control of molecules was studied, using the equation of motion for the expectation value of the operator. With this method a requisite external field was obtained to track exactly a prescribed molecular objective expectation value as a function of time. Applications to diatomic and polyatomic molecules were formulated. While the method was directly applicable as a test of physical intuition, it could, in principle, be used to design fields for specific objectives, including reactive selectivity. Results were presented for position and energy tracking in the hydrogen fluoride molecular system. The numerical calculations showed that seemingly benign objective tracks may give rise to singularities in the field. However, these singularities did not present problems in the evolution of the dynamical quantities, and instead, provided useful hints for designing robust fields.

13. **Teaching Lasers to Control Molecules in the Presence of Laboratory Field Uncertainty and Measurement Imprecision.[13]**

This study proposed an iterative optimization algorithm for designing laser fields to control molecular motion, which utilized laboratory input (test fields) and output (resulting product yields) information. Laboratory uncertainties, such as laser field noise, and limited precision in the product yield measurements were included in the simulations of the experiments. Two simulated examples of implementation of the algorithm were presented: selective electronic excitation in a model four-state system, and maximizing dissociation yield of the hydrogen fluoride molecule. Both examples demonstrated that, even with the inclusion of laboratory uncertainties, the experimental learning-based algorithm was a potential feasible method for controlling molecular motion, and possibly manipulating chemical reactions.

14. **Beyond the Bloch Equations: A Wavefunction-Based Approach to Selective Excitation in Condensed Media.[14]**

This work presented an optimization procedure for producing selective excitation of molecules undergoing stochastic dephasing collisions. The collisional effects were incorporated by propagating the Schrödinger equation with random perturbations. The optimization procedure utilized gradients of the perturbation-averaged physical objective with respect to the laser field parameters; we demonstrated on a model problem that very few averages over collisional events sufficed to yield converged results. Therefore, this method was computationally efficient because large averaging of dynamical simulations was not necessary. These results showed the viability of the optimal control procedure for application to controlling chemical reactions in solution.

15. **Paradigms and Algorithms for Controlling Molecular Motion.[15]**

The development of programmed and structured laser pulses opened up the prospect of controlling molecular motion. Recent theoretical schemes suggested to achieve this goal were

discussed in this work, and then, a general optimal control paradigm was presented, whereby field structuring to meet molecular objectives was achieved in a systematic fashion. Various examples were discussed, including control of rotational, vibrational, and electronic motion, and reactivity in triatomic photodissociation. A comprehensive algorithm was presented, drawing on the best capabilities of theoretical design tools and laboratory techniques. This algorithm suggested the possibility of achieving molecular control without *a priori* accurate knowledge of the Hamiltonian.

16. **Optimal Control of Classical Systems with Explicit Quantum/Classical Difference Reduction.[16]**

This work employed optimal control theory to design an external driving field which reduced the difference between certain quantum observables and their classical counterparts, in addition to achieving some dynamical objective. Because many different driving fields can achieve a similar target, as shown in item (5b) above, there was the flexibility of asking that the field also cause quantum and classical observations to match. Several examples were shown, using a one-dimensional model system which was highly nonclassical in the absence of a driving field. These illustrations demonstrated some of the richness of possibilities for obtaining good quantum-classical agreement for chosen observables, even in the presence of other design criteria.

17. **Control of Coherent Wave Functions: A Linearized Molecular Dynamics View.[17]**

In this study, the Schrödinger equation was linearized with regard to a low-intensity controlling electric field. For such a linearized quantum dynamical system, the study answered the issued of controllability and explicitly provided the control field. Starting in a particular eigenstate, the resultant necessary and sufficient conditions for controllability required that the system satisfy the following two criteria: (1) the N eigenstates of the field-free Hamiltonian, superimposed to form the coherent final state, must be nondegenerate, and

(2) the electric dipole transition moments, from the initial state to each of the above eigenstates, must be non-zero. The control field was obtained analytically in terms of N monochromatic electric fields, each of which had a frequency corresponding to the transitions of the field-free Hamiltonian. The study showed that the physical properties of the control field were not affected by the overall phase of the coherent wave function. Using Li_2 as an example, we investigated the control properties of creating specified coherent wave functions on the excited potential energy surface $A^1\Sigma_g^+$ by excitation from an initial state on the $X^1\Sigma_g^+$ surface. The numerical results suggested that the required control field was reasonable for laboratory realization.

18. Optimal Control of Classical Anharmonic Molecules Represented with Piecewise Harmonic Potential Surfaces: Analytic Solution and Selective Dissociation of Triatomic Systems.[18]

In this work, we applied optimal control theory to manipulate the dynamics of molecular systems with anharmonic potential surfaces modelled as a series of continuous piecewise harmonic sections within the classical approximation. In analogy to the simple harmonic case, an analytic solution was possible, yet bond dissociation was allowed. This methodology was applied to several model systems. It was found that the molecular objective of selective dissociation was achieved for a model linear triatomic system.

19. Hot Lasers - Cool Molecules.[19]

This short invited paper in *Nature*'s "News and Views" gave a summary of a *Journal of Chemical Physics* article (**99**, 196-210, 2993) and its significance to the molecular control field.

20. Optimal Molecular Control in the Harmonic Regime: The Methylene Halide Chemical Series and Fluorobenzene.[20]

In this work, optimal control theory was applied to molecules described by harmonic force fields for the purpose of selectively exciting vibrational motion. The molecular parameters were taken from experiments, where possible. The results for different targets in the methylene halide chemical series were studied, to learn how the control results track with the changing halogen constituent. It was seen that large differences in control results for different halogen constituents occur even when the target is a CH stretch. The in-plane modes of fluorobenzene were also studied, to illustrate control in a larger realistic molecule with more complex connectivity. Aspects of molecule orientation relative to electric field polarization were addressed. In addition, a novel method of displaying motion was employed.

21. An Application of Minimax Robust Optimal Control Theory for Selective Vibrational Excitation in Molecules.[21]

In recent investigations, control theory was applied to design electromagnetic fields capable of producing vibrational excitation in molecular systems. This approach has been applied to linear or non-linear classical approximations of molecular systems or to quantal systems using distributed cost functionals. Practical computations of molecular optimal control theory for large molecules, especially with anharmonic potentials, become difficult due to the increased dimensionality and the mixed nature of the boundary conditions. This work proposed to approach the control design for such systems by treating a portion of the molecule containing the target and dipole bonds in full detail, while the effect of the remainder of the system was modelled as a disturbance of limited energy. The optimal field *minimized* the cost functional, which was simultaneously *maximized* with respect to the disturbance. Such assumptions gave rise to a robust controller akin to the H_∞ theory of robust estimation. We investigated the various field designs for truncated harmonic systems associated with different disturbance energies, and demonstrated that the existence of the solution to the associated Ricatti equation ensured the existence of the equilibrium game

point. In addition, in the range of physically reasonable disturbance energy, the optimal field could be accurately predicted from an asymptotic expansion involving only the undisturbed reference case. As an application, we showed the optimal field design for a 20-atom truncated molecular chain containing both the target bond (the fifth bond) and the dipole bonds (the first and ninth bonds), where the disturbance only affected the end bond of the system attached to the remainder of the chain. In an effort to improve on the efficiency of the bond energy deposition, we investigated shortened target times, and also a 40-atom truncated chain. This approach presented very conservative estimates of possible disturbances, but provides insight into the sensitivity of different configurations with respect to external disturbances. The minimax approach can be generalized to non-linear molecular systems by modelling the original system as a linear system plus an energy constrained disturbance.

22. **Effects of the Target Time in Controlling Molecular Motion: The Role of Errors in the Field and in the Model.[22]**

This study examined the effects of random errors in the electric field, and errors inherent in the model on the choice of target time T, in designing an optimal field to achieve site-selective excitation in molecular systems. A formalism was presented for control of classically modelled systems, which included additional costs due to these errors. In applying this formalism to a linear coupled harmonic system, it was demonstrated that, for errors in the model, the additional cost terms approach asymptotic values. In contrast, for a constant magnitude of error in the field, the added terms manifested consistent growth behavior with increasing target times due to accumulation of phase errors in the controlled dynamics. It was illustrated that a reasonable level of field and force constant error had a minimal influence on the practical choice of a final target time. Although other systems may behave differently and must be assessed on their own merit, some general conclusions were drawn regarding the factors influencing the choice of a target time T.

23. Optimally Controlled Five-Laser Infrared Multiphoton Dissociation of HF.[23]

In this study, simulations of the quantum dynamics of the HF molecular immersed in a field of five overlapping, intense, linearly polarized, infrared laser pulses of subpicosecond duration were performed. The HF molecule, initially in its ground state, was modelled as a rotating oscillator interacting with a classical laser field via electric dipole interaction. Realistic potential and dipole functions were used. Optimal overlaps of the five laser pulses, as well as the optimal carrier frequencies of the laser pulses, were found which maximized the HF dissociation yield. A maximal yield of 45% in a single combined pulse was achieved using the best available potential and dipole moment functions. The optimal infrared multiphoton dissociation pathway for the HF molecule included a series of $\Delta v = 1$ vibrational-rotational transitions, followed by a series of $\Delta v \geq 2$ vibrational-rotational transitions. The latter was necessary as a consequence of the vanishing $\Delta v = 1$ transition moments around $v = 12$. In the $\Delta v = 1$ regime, both P and R branch transitions were found to be important. The angular distribution of the dissociative flux was computed. Robustness of the results, with respect to changes in the interatomic potentials, dipole functions, and reduced mass, as well as to changes in laser pulse parameters (carrier frequencies, timings, phases, field amplitudes, and pulse durations) was investigated.

24. Robust Optimal Control of Quantum Molecular Systems in the Presence of Disturbances and Uncertainties.[24]

Recently, systematic optimal control theory has been successfully applied to design optical fields which act on a molecule to guide or transform it into a specifically prescribed state. Under realistic laboratory conditions, and for real molecules, it is inevitable that there will exist disturbances and uncertainties in the control optical field, in the molecular Hamiltonian, and in the field coupling coefficient (e.g., the dipole moment), etc. Therefore, it is important to design an optimal field which is robust to disturbances. This work provided a method through which the worst possible disturbance to the control process, under certain possible

constraints, could be calculated, and a corresponding optimal control field designed to be robust to the disturbances. Under disturbances of small amplitude a perturbation solution to this problem could be applied. Illustrations were given for control of the wavepacket evolution of a diatomic molecule in the presence of disturbances.

25. Control of Quantum Dynamics: Issues and Alternatives.[25]

This work gave an overview of the logic behind current conceptual issues directed towards controlling quantum dynamics phenomena. The role of theory to translate these concepts into laboratory designs was highlighted, along with an explanation of the complexities of achieving realistic designs. As a result, it was argued that closed-loop feedback control of quantum dynamics in the laboratory was not only feasible, but was typically a necessity for the achievement of practical control over quantum phenomena.

26. Locking a Molecular Bond: A Case Study of CsI.[26]

This research treated the problem of locking a molecular bond at a length other than the equilibrium distance, with the help of optical electric fields. Locking conditions for single-color fields were examined, and slowly decaying locked wave functions were sought. These wave functions were then used as target functions in an optimal control procedure. The resultant solution was an optimal field that created a wave functions as close as possible to the target function, followed by the application of a locking single-color field that kept a large part of this wave function at the given position. An objective of this approach was to eventually extend the optimal control theory to the preparation of molecules in quasi-stationary nonequilibrium states, for further study by spectroscopic or other means. Results were reported for a model of CsI with two potential energy surfaces, one with a repulsive character.

27. Optimal Control of Classical Molecular Dynamics: A Perturbation Formulation and the Existence of Multiple Solutions.[27]

This research considered the prospect for there being multiple solutions to the control of classically modelled molecular dynamical systems. The research followed up on a parallel study based on quantum mechanics. For polyatomic molecules, it is generally expected that a classical mechanical model will be adequate and necessary as a means for designing optical fields for molecular control. The prospect of multiple control field solutions existing in this domain was important to establish, in terms of ultimate laboratory realization of molecular control. A general formulation of the multiplicity problem was considered, and the existence of a denumerably infinite number of solutions for the control field amplitude was shown to be the case under certain mild limitations on the physical variables.

28. Simulator of Optimally Controlled Molecular Motion.[28]

In this work, we presented results of a molecular dynamics simulator (MDS) used to explore optimal control of molecular motion. A realistic model of an interatomic potential was created by a configuration of magnets. This simulated potential approximately modelled both the short and long range portions of true molecular potentials. Atoms within a polyatomic molecules were simulated using carts which floated on an air track, and a mechanical driver simulated the action of a controlling laser. In analogy with a molecular system, the potential was determined by analysis of a series of dynamics experiments. Knowledge of the potential, combined with optimal control theory, enabled the design of the driver motion necessary to achieve controlled dissociation. Successful control required overcoming a variety of difficulties analogous to those expected to be faced in the control of true molecular systems. The MDS provided insight into factors affecting the molecular control, by demonstrating a real-time simulation of laser-controlled molecular dynamics.

29. Display of the Flow of Energy in Molecules.[29]

This research resulted in the development of a method to graphically display the flow of energy within molecules. An energy continuity equation was derived, leading to a molecular energy flux vector field. Computation of the flux called for the intramolecular potential, any external interactions, and the phase space trajectories of the molecular motion. The flux provided a means to display energy flows in still frames, and as a tool to visualize hitherto undiscovered dynamic pathways in molecules. Examples were presented that showed energy flow in three molecular systems, and illustrated the point that depiction of energy flux patterns has increasing utility and meaning as one moves to larger molecules. Simple extensions to this work would also allow visualization of the flux of such quantities as linear and angular momentum.

30. A New Approach to Molecular Classical Optimal Control: Application to the Reaction HCN → HC+N.[30]

In this work, we presented a new method for classical control theory of Hamiltonian systems. This approach was based on a special treatment of the adjoint or Lagrange multiplier equations of motion. The latter function is only asked to preserve the mean of the ensemble of molecular trajectories. In this case, only four such equations are involved, greatly simplifying the field design process, and making it faster and more stable. Good results were obtained for the selective photodissociation of HCN. The objective was to control the intramolecular reaction HCN → HC + N (i.e., break the stronger bond). Hamilton's equations of motion were employed to model the HCN molecule, initially in its ground state. The control equations are integrated to obtain a high degree of selectivity in the unimolecular dissociation. The robustness of the results to changes in the initial conditions and pulse durations were investigated. An increase of the pulse duration beyond a certain point made it more difficult to dissociate the N atom, due to strong intramolecular coupling.

The resultant pulse fields may serve as a basic indicator for future experimental selective dissociation of HCN $\rightarrow$ HC + N, using higher power lasers.

31. Adaptive Feedback Control of Molecular Motion.[31]

Control of molecular -scale events, including chemical reactions has long been a sought-after goal. A central problem is to design control fields such that particular molecular objectives are achieved while suppressing undesirable processes. The techniques of optimal control theory within quantum mechanics provided the framework for carrying out the designs. By replacing the model of the molecules in the computer with the actual molecule in the laboratory, various design problems were overcome. In this fashion, the molecule acted as an analog computer, to solve its own dynamical equations in appropriate pump-probe experiments performed iteratively, and guided by a learning algorithm, to ultimately achieve the desired molecular control objective. The practicality of this approach, and some future directions of the field were also discussed.

32. Optimal Control of Chaotic Hamiltonian Dynamics.[32]

Two general methods were developed to optimally control chaotic dynamics. The first method consisted of self-consistently seeking a path, defined by the average trajectory of the achieved control and drawing in the irregular trajectories around the average trajectory. The second method aimed for the same goal, except with an imposed regular fiducial trajectory. These two methods were complementary in their approaches to achieving control over chaotic behavior. A Lagrange multiplier technique and penalty method were used in the process of finding the optimal solution that minimizes a cost functional. Approximations were introduced for the Lagrange multipliers, based on preserving and controlling only the average trajectory. The optimal external control field $\epsilon(t)$ influenced the chaotic trajectories by redirecting them to a region in the phase space, where it was possible to maintain a tight bundle of trajectories with a minimum external interaction. Also, the results showed that the

interaction energy was small in comparison with the total energy of the system, indicating an efficient control strategy.

33. Controllability of Molecular Systems.[33]

In this work, we analyzed the controllability of quantum systems arising in molecular dynamics. We modelled these systems as finite level systems, and examined their controllability. To do this, we passed to their unitary generators and used results on the controllability of invariant systems on Lie groups. Examples of molecular systems, modelled as finite-dimensional control systems, were provided. A simple algorithm to detect the controllability of a molecular system was provided. Finally, we applied this algorithm to a model five-level system.

34. Optimal Control of Molecular Motion for δ-Target Probability Density.[34]

This work presented a new δ-target approach to solving the problem of steering a molecular system to a desirable geometrical configuration by an electromagnetic field. The δ-target technique was shown to provide good control, and the advantages of the δ-target approach were analyzed. In particular, in the weak field limit, the computational difficulties were considerably simplified; the control problem reduced to a task of propagating the δ-target wave function, with the Hamiltonian of the molecular system independent of time. This simplification was of principal importance, as it permitted applications of optimal control theory to chemically interesting larger molecular systems.

35. Determining Regular Orbits in the Presence of Irregular Trajectories Using Optimal Control Theory.[35]

Two general algorithms were presented in this work, to determine regular orbits in the presence of irregular trajectories in a phase space of n degrees of freedom. The first algorithm searched for regular orbits with the energy as a free-floating parameter. The

second algorithm sought regular orbits at constant energy. These two approaches utilized optimal control theory to employ a small external control field that permitted a search among the irregular motion for the regular orbits. The optimizing algorithm naturally sought regular orbits with the control field turned off. Numerical results with a chaotic Hamiltonian showed the method to be effective in determining regular trajectories. If the system is completely chaotic in some region, the method determined which initial condition was the best one in order to achieve a nearly regular orbit.

36. Competitive Tracking of Molecular Objectives Described by Quantum Mechanics.[36]

The control of molecular events by optical fields was sought with the methods of asymptotic inverse tracking, local track generation (model matching), and competitive tracking, which are extensions of exact inverse tracking. The methodology was applied to infrared dissociation of a diatomic molecule, and selective dissociation of the stronger bond in a highly coupled linear triatomic system. The major appeal of these methods is that they do not require costly iterations, unlike other control approaches in which optimization techniques are used to design fields to achieve desired molecular objectives. It was found that in *exact* inverse tracking, where a requisite external field was obtained to exactly track a prescribed objective expectation value as a function of time, a high degree of intuition was required to find an *a priori* objective track, such that the required fields were reasonable in terms of intensity and bandwidth. Furthermore, exact inverse tracking does not allow for tracking of multiple observables. The extensions of the inverse tracking method presented in this study helped to alleviate these drawbacks. In all of these extensions, the requisite field was computed locally in time, through minimization of a cost functional which contained terms designed to minimize the error between the objective and actual tracks, and also minimize the field fluence. The objective tracks could be prescribed *a priori*, as in exact inverse tracking or from the evolving system state (local track generation). Competitive tracking allowed for

the following of multiple observables, although none were tracked exactly. Locally generated tracks (model matching) required less physical intuition because it was easier to specify an objective track with current knowledge of the state of the system. However, the trade-off with this method was that prediction of the behavior of the tracked observables might be elusive.

37. Control of Molecular Motion.[37]

This work was an invited manuscript to the *Proceedings of the IEEE*. The paper was requested as a result of the traditional engineering control community expressing curiosity about active control research under way at the molecular scale. The work aimed to present a synopsis of some of the key issues, in a context relevant to the control engineering community. Similarities and distinctions between molecular control and traditional engineering control were highlighted. Particular emphasis was also given to some of the key mathematical aspects of the subject, and areas where further study was warranted.

ARO-SUPPORTED PUBLICATIONS RESULTING FROM THIS RESEARCH

1. Optimal Control of Nonlinear Classical Systems with Application to Unimolecular Dissociation Reactions and Chaotic Potentials, C. Schwieters and H. Rabitz, *Phys. Rev. A*, **44**, 5224 (1991).

2. Optimal Control of Molecular Motion: Making Molecules Dance, H. Rabitz and S. Shi, in *Advances in Molecular Vibrations and Collision Dynamics*, edited by Joel Bowman, Vol. 1, Part A, 187 - 214 (JAI Press, Inc., 1991).

3. Optimal Control of Molecular Motion, H. Rabitz, in *Coherence Phenomena in Atoms and Molecules in Laser Fields*, edited by A.D. Bandrauk and S.C. Wallace, Plenum Publishing Corporation, New York (1992), p. 315.

4. Optimal Control of Selectivity of Unimolecular Reactions Via An Excited Electronic State with Designed Lasers, S. Shi and H. Rabitz, *J. Chem. Phys.*, **97**, 276 (1992).

5. Robust Optimal Control Theory for Selective Vibrational Excitation in Molecules: A Worst Case Analysis, J.G.B. Beumee and H. Rabitz, *J. Chem. Phys.*, **97**, 1353 (1992).

6. Application of the Born-Oppenheimer Principle to Classification of Time Scales in Molecules Interacting with Time-Dependent External Fields, T. Gil, S. Shi, A. Askar, and H. Rabitz, *Phys. Rev. A*, **45**, 6479 (1992).

7. Optimal Control of Curve-Crossing Systems, P. Gross, D. Neuhauser, and H. Rabitz, *J. Chem. Phys.*, **96**, 2834 (1992).

8. Coherent Control of Quantum Dynamics: The Dream is Alive, W.S. Warren, H. Rabitz, and M. Dahleh, *Science*, **259**, 1581 (1993).

9. Optimally controlled quantum molecular dynamics: A perturbation formulation and the existence of multiple solutions, M. Demiralp and H. Rabitz, *Phys. Rev. A*, **47**, 809 (1993).

10. Optimally controlled quantum molecular dynamics: The effect of nonlinearities on the magnitude and multiplicity of control-field solutions, M. Demiralp and H. Rabitz, *Phys. Rev. A*, **47**, 831 (1993).

11. Optimal Control of the Electric Susceptibility of a Molecular Gas by Designed Non-resonant Laser Pulses of Limited Amplitude, L. Shen, S. Shi, C. Lin, M. Littman, H. Rabitz, J.P. Heritage, and A.M. Weiner, *J. Chem. Phys.*, **98**, 7792 (1993).

12. Inverse Quantum-Mechanical Control: A Means for Design and a Test of Intuition, P. Gross, H. Singh, H. Rabitz, K. Mease, and G.M. Huang, *Phys. Rev. A*, **47**, 4593 (1993).

13. Teaching lasers to control molecules in the presence of laboratory field uncertainty and measurement imprecision, P. Gross, D. Neuhauser, and H. Rabitz, *J. Chem. Phys.*, **98**, 4557 (1993).

14. Beyond the Bloch Equations: A Wavefunction-Based Approach to Selective Excitation in Condensed Media, P. Gross, D. Neuhauser, and H. Rabitz, *J. Chem. Phys.*, **98**, 9650 (1993).

15. Paradigms and Algorithms for Controlling Molecular Motion, D. Neuhauser and H. Rabitz, *Accounts of Chemical Research*, **26**, 496 (1993).

16. Optimal Control of Classical Systems with Explicit Quantum/Classical Difference Reduction, C.D. Schwieters and H. Rabitz, *Phys. Rev. A*, **48**, 2549 (1993).

17. Control of Coherent Wave Functions: A Linearized Molecular Dynamics View, L. Shen, S. Shi, and H. Rabitz, *J. Phys. Chem.*, **97**, 8874 (1993).

18. Optimal Control of Classical Anharmonic Molecules Represented with Piecewise Harmonic Potential Surfaces: Analytic Solution and Selective Dissociation of Triatomic Systems, M.H. Lissak, J.D. Sensabaugh, C.D. Schwieters, J.G.B. Beumee, and H. Rabitz, *Chem. Phys.*, **174**, 1 (1993).

19. Hot Lasers - Cool Molecules, H. Rabitz, *Nature*, **366**, 304 (1993).

20. Optimal Molecular Control in the Harmonic Regime: The Methylene Halide Chemical Series and Fluorobenzene, C.D. Schwieters and H. Rabitz, *J. Phys. Chem.*, **97**, 8864 (1993).

21. An Application of Minimax Robust Optimal Control Theory for Selective Vibrational Excitation in Molecules, J.G.B. Beumee and H. Rabitz, *J. Math. Chem.*, **14**, 405 (1993).

22. Effects of the Target Time in Controlling Molecular Motion: The Role of Errors in the Field and in the Model, A. Michaels, C. Schwieters, and H. Rabitz, *J. Phys. Chem.*, **98**, 2508 (1994).

23. Optimally Controlled Five-Laser Infrared Multiphoton Dissociation of HF, M. Kaluza, M.T. Muckerman, P. Gross, and H. Rabitz, *J. Chem. Phys.*, **100**, 4211 (1994).

24. Robust Optimal Control of Quantum Molecular Systems in the Presence of Disturbances and Uncertainties, H. Zhang and H. Rabitz, *Phys. Rev. A*, **49**, 2241 (1994).

25. Control of quantum dynamics: issues and alternatives, H. Rabitz, in *Laser Techniques for State-Selected and State-to-State Chemistry II*, SPIE Proceedings, **2124**, 84 (1994).

26. Locking a molecular bond: A case study of CsI, T. Szakács, B. Amstrup, P. Gross, R. Kosloff, H. Rabitz, and A. Lörincz, *Phys. Rev. A*, **50**, 2540 (1994).

27. Optimal Control of Classical Molecular Dynamics: A Perturbation Formulation and the Existence of Multiple Solutions, M. Demiralp and H. Rabitz, *J. Math. Chem.*, **16**, 185 (1994).

28. Simulator of optimally controlled molecular motion, D. Morris, C. Schwieters, M. Littman, and H. Rabitz, *Am. J. Phys.*, **62**, 817 (1994).

29. Display of the Flow of Energy in Molecules, C.D. Schwieters and H. Rabitz, *J. Comp. Chem.*, **15**, 80 (1994).

30. A new approach to molecular classical optimal control: Application to the reaction HCN → HC+N, J. Botina, H. Rabitz, and N. Rahman, *J. Chem. Phys.*, **102**, 226 (1995).

31. Adaptive Feedback Control of Molecular Motion, H. Rabitz, in *Frontiers of Chemical Dynamics* (Proceedings of NATO - ASI Frontiers of Chemical Dynamics Conference, Antalya, Turkey, September 4 - 16, 1994), edited by E. Yurtsever, p. 181, (Kluwer Academic Publishers, The Netherlands, 1995).

32. Optimal Control of Chaotic Hamiltonian Dynamics, J. Botina, H. Rabitz, and N. Rahman, *Phys. Rev. A*, **51**, 923 (1995).

33. Controllability of Molecular Systems, V. Ramakrishna, H. Rabitz, M.V. Salapaka, M. Dahleh, and A. Peirce, *Phys. Rev. A*, **51**, 960 (1995).

34. Optimal Control of Molecular Motion for δ-Target Probability Density, V. Dubov and H. Rabitz, *Chem. Phys. Lett.*, **235**, 309 (1995).

35. Determining regular orbits in the presence of irregular trajectories using optimal control theory, J. Botina, H. Rabitz, and N. Rahman, *J. Chem. Phys.*, **103**, 6637 (1995).

36. Competitive tracking of molecular objectives described by quantum mechanics, Y. Chen, P. Gross, V. Ramakrishna, H. Rabitz, and K. Mease, *J. Chem. Phys.*, **102**, 8001 (1995).

37. Control of Molecular Motion, M. Dahleh, A. Peirce, H. Rabitz, and V. Ramakrishna, *Proceedings of the IEEE,* **84**, 7 (1996).

SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT
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1. Jair Botina, Visiting Research Associate and Post-Doctoral Associate

2. Metin Demiralp, Visiting Research Scientist

3. Valery Dubov, Post-Doctoral Associate

4. Peter Gross, Ph.D. awarded

5. Daniel Morris, Undergraduate

6. Herschel Rabitz; Principal Investigator

7. Charles Schwieters; Ph.D. awarded

8. Liyang Shen, Ph.D. awarded

9. Harjinder Singh, Post-Doctoral Associate

10. Hong Zhang; Post-Doctoral Associate